Journal of Mines and Geosciences
ISSN 3057-3483

The Role of Minerals on Petroleum Generation: An implication for the pyrolysis of Asphaltene from Bitumen

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Keywords

Minerals;
Petroleum Generation;
Asphaltene;
Pyrolysis;
Pyrite;
Silica;

Article information

Submitted:
24th February 2024
Reviewed:
30th September2024
Accepted: 4th Nov 2024
Publ: 21st Nov 2024

Abstract

This laboratory study replicates natural petroleum generation processes using analytical pyrolysis techniques applied to sedimentary organic matter. We focus on assessing pyrite and silica's roles in petroleum formation by analyzing changes in pyrolysate during analytical pyrolysis. We vary temperature (750°C to 1000°C) and heating time (8 to 15 seconds) as key factors to relate with the natural petroleum generation processes which consider the duration or time of decomposition of organic matter with temperature.

Asphaltene is employed as a primary component to simulate petroleum product generation. We investigate asphaltene's thermal degradation behavior and physical characteristics, extracting it from bitumen samples using n-hexane. Pyrite (FeS_2) and silica (SiO_2) minerals are matrix feedstock or adsorbent. A pyrolysis gas chromatography-mass spectrometry (Py-GC/MS) is an essential tool for identifying pyrolysates. Our study highlights significant aliphatic chain products such as n-alkanes and n-alkenes up to C_{32} in asphaltene from an Iraq bitumen sample. Notable, the heavy hydrocarbons in the pyrolysate are aromatic.

Our results show differing mineral effects on pyroproducts, with silica's impact minimal compared to pyrite's substantial catalytic influence on asphaltene pyrolysis. Pyrite adsorbent notably generates around 10 times more methane gas (CH4) than silica adsorbent, emphasizing pyrite's catalytic role in pyrolysis. Methane gas production is attributed to a free radical mechanism during thermal cracking. Prolonged heating of asphaltene samples containing pyrite enhances the production of hydrocarbon aliphatic chain products. This study highlights the significant influence of minerals on pyrolysis, particularly the catalytic effects of pyrite on asphaltene pyrolysis and the generation of pyrolysate, with notable evidence of methane gas production. Coal was used in this study solely to compare decomposition peaks, as it shares similar structural and behavioral characteristics with asphaltene.

1. Introduction

1.1 Background Introduction

This study is an extract from the master of science dissertation work of the first author entitled matrix feedstock interaction during analytical pyrolysis which was submitted at the University of Aberdeen in the United Kingdom in 2015. It forms part of the synthesis work of a laboratory approach to simulating the natural petroleum generation processes. The maturation and thermal decomposition of organic matter were tested in the laboratory considering time and temperature. To access the catalytic effects of minerals during the decomposition of organic matter; silica and pyrite minerals were used as adsorbent. Organic geochemistry can be used as a powerful tool to clarify the origin and modernization of the geological history of organic matter in the geosphere (Rubinstein et al., 1978). The analytical pyrolysis techniques for petroleum generation can be simulated in the laboratory to reflect the natural processes of generating petroleum through the pyrolysis of sedimentary organic matter. Preparative practices differ and the organic component may or may not be isolated before pyrolysis. The effects of mineral matrices on the formation of natural gases and crude oils have been extensively examined and taken as necessary controls on the processes of hydrocarbon generation. They have also been considered in the evolution of oil and gas resources (Ma et al., 2016). This study has investigated the mineral matrix effects with minimum samples of asphaltenes and minerals. Analytical Py – GC – MS is broadly applied in various disciplines of research and development of new materials, geology, environmental science (biology) and biotechnology, airspace, quality control, drugs or medicine, ecological or environmental analysis to forensic intentions, categorization and competitor product assessment, preservation and reinstatement of cultural heritage (Kusch, 2012). It is also the analytical technique of preference for the identification of biomarker compounds present in organic mixtures extracted from environmental, biological, and geological samples (Medeiros and Simoneit, 2007). For comparison purposes, a coal sample was decomposed for correlation of peaks with asphaltene due to their similarity in structural and behavior properties (Calemma et al., 1997).

1.2 Source of Bitumen and Asphaltene

Bitumen samples collected from the Zagros Thrust Belt (Agra anticline) in the Kurdistan region in Northern Iraq were used in this study. The natural bitumen samples were taken from dolomitic limestone voids of the Agra anticline. Firoozifar et al. (2011) defined bitumen as a thermoplastic material that is an elastic solid at relatively low temperatures and becomes a viscous liquid at extremely high temperatures. It is also defined as the heaviest form of petroleum which is the residue of the secondary microbiological degradation of conventional petroleum (Strausz and Lown, 2003; Strausz et al., 2010). The fractions of bitumen are hydrocarbons, resins, and asphaltene. They are slightly viscoelastic, dense, semi-solid hydrocarbons with a dark brown to black color containing heteroatoms such as nitrogen, oxygen, and sulfur with trace-level metals and organometallic compounds (Strausz and Lown, 2003; Strausz et al., 2010). Asphaltenes are regarded as soluble components of kerogen (Behar et al., 1984; Geng and Liao, 2002) and are considered to be similar to the most labile part of the respective kerogen in the oil reservoirs (di Primio et al., 2000; Geng and Liao, 2002; Sarmah et al., 2010) forms a significant constituent of crude oil. Asphaltene extracted from the Zagros bitumen sample was collected and used for this work. Asphaltenes are defined based on solubility criteria and the characterization of their structural configuration has been broadly investigated by several physical and chemical analytical methods (Calemma et al., 1997). In other ways, asphaltene can be categorized as a class of material of considerable importance in refining processes since its presence may cause some problems in the thermal and catalytic transformation of petroleum residue (Goncalves et al., 2001). Many researchers' results indicated that asphaltenes are a complex polydispersed mixture of molecules with an average molecular weight ranging between 1500 and 4000 consisting of aromatic and hydroaromatic units of various condensation degrees and the joining units are aliphatic bridges bearing alkyl side chains made up of 25 – 30 carbon atoms (Calemma et al., 1997).

1.3 Analytical pyrolysis of asphaltene

The thermal decomposition of asphaltene may occur through three main reaction pathways which include the breakdown of aliphatic bridges between aromatic/hydroaromatic/naphthenic units, breaking off of alkyl side chains on aromatic rings, and aromatization of hydroaromatic structures (Calemma et al., 1997). Due to poor or lack of volatility and because of high molecular weight, the analysis of asphaltenes by traditional gas chromatography (GC) in their normal state becomes difficult. However, macromolecules can be heated to a temperature above 500° C to pyrolyze them into individual fragments which can be chromatographically separated and identified by mass spectrometry (Kusch, 2012). Asphaltene thermal degradation results from free radical reactions induced by bond breakup, but bond breaking depends on the strength between molecules (Kusch, 2012). The asphaltene thermal cracking follows the free radical reactions mechanism which involves a sequence of elementary steps that includes initiation, hydrogen abstraction, β scission, and termination (AlHumaidan et al., 2015). Pyrolyser needs to have accurate control of heating rate, temperature, and time to achieve quantitative reproducibility (Kusch, 2012). Therefore, according to Kusch 2012 when two or more samples of similar composition are heated at the same rate, same temperature, and for the same duration of heating (time) will produce equal or similar decomposition products. During analytical pyrolysis, the final pyrolysis temperature, rapid temperature rise, and accurate temperature control are requirements of the instrument setup.

1.4 Pyrolysis equipment setup and functions

The pyrolysis system is categorized into two groups depending on the heating mechanism; one is the continuous-mode pyrolyzer (Furnace pyrolyzer) and the other one is the pulse-mode pyrolyzer (Flash pyrolyzer) such as heated filament, curie-point and laser pyrolyzer (Kusch, 2012). The latter mode with heated platinum filament was used and the sample was put in the quartz tube. The pyroprobe was directly connected to the injector port of the GC and a flow of helium gas flushed the pyrolysates into the capillary column. When compared with kerogen, the kinetic studies of asphaltenes are rare (Geng and Liao, 2002) and most previous works on the pyrolysis of asphaltenes mainly focused on the elucidation of their structures and the identification of fragmented products based on pyrolysis temperature only with insignificant information on product fractions based on both time and temperature (Geng and Liao, 2002). In this work, both time (duration of heating) and temperature (pyroprobe temperature) were considered in discussing different matrix-feedstock on asphaltenes pyrolysis products (pyrolysate). Pyrolysis began immediately and pyrolysates were directly introduced into the capillary column for separation. The column pressure functionality was checked by ensuring that the pressure dropped when the interface was opened and raised again when the probe was in place. The whole interface was covered with aluminum foil to preserve heat and prevent draughts from cooling the interface. The interface was connected to a compressed air cylinder which fastens the cooling of the interface after each run. The tube was reweighed after pyrolysis to determine the amount of sample pyrolyzed.

The polar fractions comprising the asphaltenes remained unaltered after pyrolysis as verified by elemental and gravimetric analysis (Rubinstein et al., 1977, 1978) and hence provide important information on their source rock (Ekweozor, 1986; Geng and Liao, 2002; Rubinstein and Strausz, 1979). It is difficult to exclude asphaltenes as the source for secondary hydrocarbon generation especially when appropriate geological settings are available because they are less polymerized and aromatized than kerogen as revealed by their high H/C and low O/C atom ratios (Behar et al., 1984; Geng and Liao, 2002; Sweeney et al., 1995). Due to the existing physical and chemical relationship between petroleum asphaltenes and oil-forming kerogen; studies on asphaltenes remain a crucial aspect for the provision of better knowledge on their role played in petroleum generation, migration, and maturation. With that school of thought, asphaltenes will continue to rise as frontier molecules (molecular complex) in geochemical investigations as they give important indications concerning the nature and source of organics, migration, maturation, and secondary alteration effects (Sarmah et al., 2010).

1.5 Asphaltenes sensitivity to separation techniques

In this study, pyrolysis – GC/MS was used as a destructive analytical technique to distinguish asphaltene products produced from quartz/silica and pyrite matrix feedstock or adsorbent. The pyrolysis mechanism of asphaltene which involves the breakdown of large complex molecules into smaller molecules by the use of heat is considered to be very similar to catagenesis processes where the cracking of kerogen results in the conversion of organic kerogens into hydrocarbons. Smaller molecules are formed through cracking with a progressive increase in temperature and the cracking rate can be affected by the general composition of asphaltene due to influences on the radical initiation and propagation reactions (Killops and Killops, 2013). The formation of new molecules highly depends on the hydrogen transfer reactions similar to those observed during catagenesis (Fig. 1). Thermal disintegration progresses through radical formation and the high reactivity of radicals tends to initiate frequent repeated and parallel reactions. The product distribution models especially for n-alkane imply a free radical mechanism that involves chain reactions that cover initiation, propagation, and termination processes (Killops and Killops, 2013). During pyrolysis, asphaltene compounds were degraded at different rates but only a few compounds continue to exist in an identifiable form. In the process, biochemical changes in gases like CH_4, CO_2, H_2S, N_2O, N_2, and NH_3 can also be generated with a loss of functional groups (Killops and Killops, 2013). Methane gas can be generated by a cleavage of C - C bonds during hydrocarbon cracking and it needs less energy to break a 12C – 12C bond compared to a 13C – 12C bond (Killops and Killops, 2013).

1.6 Geochemistry of elemental composition related to asphaltene and the catalytic effects of minerals

Nitrogen, sulfur, and oxygen compounds are present in variable quantities in the aromatic hydrocarbon portion of asphaltene but are often rarely detected/abundant than the main hydrocarbons such as benzene, naphthalene, phenanthrene, and their alkylated derivatives because are found to be highly resistant to many secondary alteration processes (Killops and Killops, 2013). Pyrite being a transition metal potential for natural gas generation and sulfur, is a unique active element that is a key factor in the formation of low-matured crude oils and this makes pyrite have significant effects on hydrocarbon generation (Ma et al., 2016). The pyrite could directly influence both the evolution of gases (C2 – C5) and the generation of hydrocarbons associated with H_2S production through low valence sulfur species and whether endogenous or exogenous can enhance conversion and improve quality under hydro-liquefaction conditions (Ma et al., 2016). In the kerogen hydrous pyrolysis, the amount of methane and carbon dioxide gases produced are higher in the presence of pyrite compared to its absence and increase with the addition of iron-bearing mineral mixtures like Fe_2O_4, FeS_2, and FeS (Ma et al., 2016).

With the combination of pyrite which contain also sulfur, the alkyl chains are connected to asphaltene nuclei by C - S and S - S bonds which are considerably weaker than the C - C and C - O bonds (del Rio et al., 1993). Killops and Killops, 2013 reported that the lower temperature was sufficient to generate products and the breaking of weaker S - bonds often associated with larger fragments than normal as seen in this study in pyrolysates of asphaltene adsorbed on pyrite. Different researchers suggest that the emerging sulfur that is generated during the conversion of pyrite to pyrrhotite is at least partially accountable for the increase of the free radical concentrations though conflicting with other findings as to whether the pyrrhotite formed in the pyrite-pyrrhotite conversion and more precisely their nature have significant catalytic activity (Srinivasan, G., and Seehra, M. S.1983). According to Ma et al., 2016, the bitumen concentration increases with pyrite adsorbent than without pyrite and this implies higher maturation rates in pyrites.

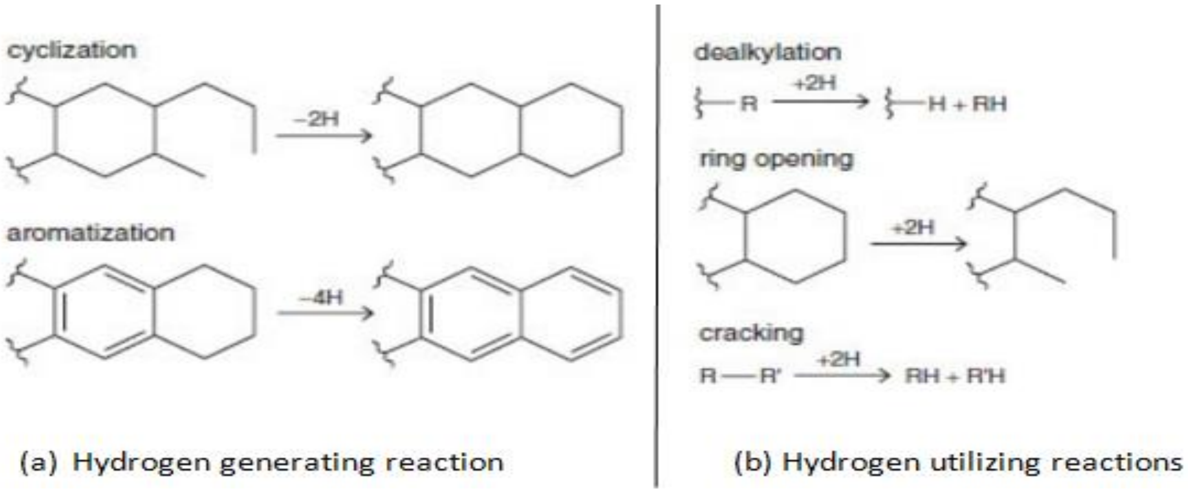


Figure 1: Hydrogen transfer reactions during pyrolysis for both hydrogen-generating and utilizing reactions (after Killops and Killops, 2013)

2. Materials and Methods

In this study, samples of asphaltenes extracted from similar bitumen were adsorbed onto silica gel and powdered pyrite minerals and then subjected to pyrolysis gas mass chromatography-mass spectrometry (Py – GC – MS - Agilent Technologies). N-hexane was used as an extracting solvent. The ChemStation software was employed for data processing and interpretation with support from the mass spectra library (NIST 05 and Wiley) and literature data. The pyrolysis data were analyzed to explore the potential for different mineral feedstock interactions or adsorption. The total ion chromatograms (TIC) were also compared with the blank chromatograms of individual minerals to identify any blank peak/contaminant in the pyrolysis products chromatograms (Fig. 4 and 5).

2.1 Extraction of asphaltene from bitumen

The naturally occurring bitumen samples from dolomitic limestone voids of the Zagros Thrust belt of Kurdistan in Iraq were provided by Ayad N. Faqi, a PhD student at the University of Aberdeen. Enough amount of bitumen sample was first broken down into small pieces and put into a vial; dissolved by dichloromethane (DCM) and/or the mixture of dichloromethane and hexane (DCM: HEX). When the bitumen was completely dissolved in DCM; a solvent n-hexane was added to the solution to precipitate asphaltene from other components such as the bitumen solution. The mixture with asphaltene precipitate was cooled (put in a fridge) overnight to facilitate precipitation further. N-hexane was regularly removed and a new n-hexane was added for at least 2-3 hours intervals until satisfactory asphaltene had precipitated.

2.2 Adsorption of asphaltene sample on silica gel and pyrite

To study the kinetic effects of asphaltene decomposition on silica gel and pyrite minerals, the asphaltene sample was adsorbed on both silica gel (60 - 120 mesh) and pyrite minerals in powder form (less than 845 µm). Ideally, between 0.5 mg to 1 mg of asphaltene was adsorbed on 5 mg to 10 mg of each silica and pyrite. The two samples; one containing asphaltene on silica and the other asphaltene on pyrite, were then dried using a hot plate heater at a temperature below 250° C to avoid asphaltene decomposition.

2.3 Pyrolysis – Gas Chromatography – Mass Spectrometry (Py-GC-MS)

2.3.1 Sample preparation before pyrolysis

The quartz tube (2.5 cm length) was used to put the adsorbed samples for pyrolysis. The bottom end of the quartz tube was filled with a small piece of glass wool; a small amount of asphaltene adsorbed sample (30 - 170 mg) for both silica and pyrite was put in the quartz tube filled about two-thirds of the tube and then the other end of the tube was covered with a piece of glass wool to keep the sample in place. The tube was weighed before and after putting the sample before pyrolysis to enable calculations of the mass of the sample used.

2.3.2 Flash pyrolysis- Gas Chromatography – Mass Spectrometry (PY-GC-MS)

Gas chromatography-mass spectrometry (GC-MS) analysis was carried out with a system consisting of the special device (CDS1000 pyroprobe analytical) which was used as a temperature programmer coupled to the Hewlett-Packard 5890 series II (HP5890) gas chromatograph equipped with a capillary column 30 m long, 0.25 mm i.d., 0.25 um film thickness, HP - 1 ms column which is connected to an HP5972 Mass Selective Detector (MSD). Helium was used as a carrier gas@ circa 1ml per minute flow rate at a split ratio of 1:100. The initial column temperature was -50o C for 2 minutes, the GC injector temperature was 310o C, the temperature program was 5.0o C per minute the maximum oven temperature was 325o C due to restricted thermal stabilities of capillary column and stationary phase. The oven temperature was set to 60o C after each run to prevent the automatic cooling of the GC to -50o C. Two data acquisition modes were used; one was a full scan mode which was only done for coal samples to support asphaltene peak product identification and interpretation and the other method was a Selected Ion Monitoring (SIM) mode. The SIM ions selected were 15, 27, 41, 42, 43, 71, 83, 85, 91, 92, 113, 128, 142, 178 and 192 m/z ions. The analysis time for one sample was 122.50 minutes. The acquired data were processed in the Scan and SIM modes supported with HP ChemStation software and the compounds/peaks identification was done based on comparison with coal pyrolysis peaks, Peaks identification of MS fragmentation patterns, was based on published data and the comparison of retention times (sometime the retention time may not be precise) of observed peaks with those of standard. The interface temperature was 330° C with a ramp rate of 5° C/min, the programmed temperature varied from 750° C to 1000° C and the holding time ranged from 8 seconds to 15 seconds. The quartz tube containing the sample was then carefully placed in the platinum coil of the probe and put in the probe interface. Once the sample was interfaced to the GC, the interface temperature was raised to 280° C and instantly started cooling the oven from ambient (60° C) to -50° C then pyrolysis was activated by just pressing the start button on both the GC and the pyroprobe.

2.3.3 Pyrolysis of coal sample

Since asphaltene and coal have similar structural and decomposition behavior (Calemma et al., 1997). A coal sample was used for reference of its pyro products. For better identification of compounds in the resulting pyrograms of asphaltene and comparison purposes; a coal sample was first pyrolyzed and then used as a reference or standard for peak identification of the resulted pyrolysates (Calemma et al., 1997).

3. Results and Discussion

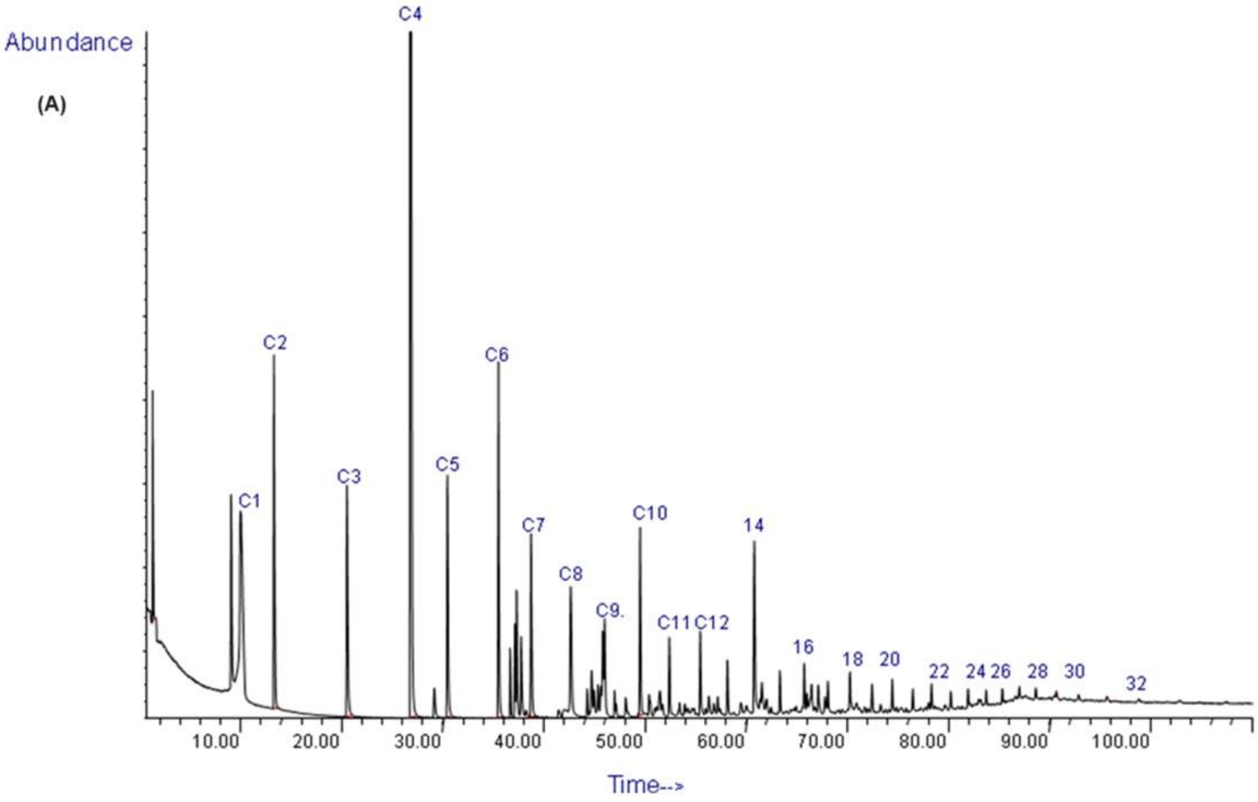
3.1 Pyrolysis products of asphaltene adsorbed on silica and pyrite

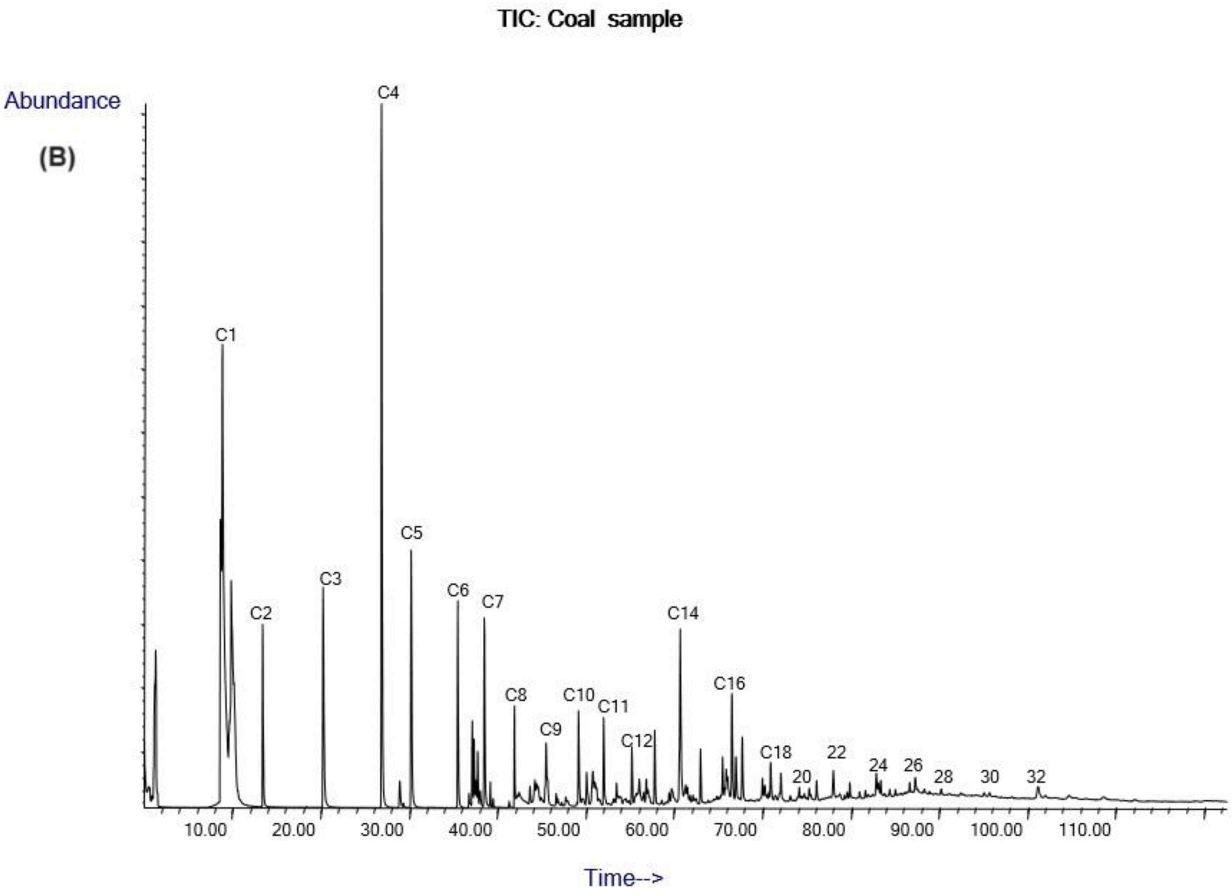
The identified compounds include hydrocarbons ranging from C1 to C32 n-alkanes; n-alkenes and aromatic. The light hydrocarbon gases (C1 - C4) were identified by m/z 15, 27, 42, 43. Hexane by m/z 41, decane (m/z 71), n-alkenes (m/z 83), n-alkanes (m/z 85), alkyl benzene derivatives such as xylene/toluene or ethyl benzene (m/z 91, 92). Acyclic isoprenoids – pristane were identified by m/z 113, naphthalene, and alkyl naphthalene derivatives-methyl naphthalenes by m/z 128 and 142 (Fig. 3).

The observed variations in chain length of the n-alkane and n-alkenes series offer evidence for polydispersity of the alkyl substituents that exist in the asphaltene structure. Calemma et al., 1997 investigated seven asphaltenes upon pyrolysis and obtained about 80 % fraction of iso-alkanes, n-alkanes (C5 - C26), the corresponding l-n alkenes (C5 – C20) and the benzene mono and poly substituted with aliphatic chains up to C4 – C5 while the remaining 20 %

consisted polyaromatic compounds mainly naphthalene bearing alkyl groups, sulfur heterocyclic compounds (alkyl substituted benzothiophene like structures) and cycloalkanes. These results resemble the pyrolysate of asphaltenes isolated from ancient crude oils of East Siberia which included the homologous series of C7 - C35 n-alkanes and n-alkenes as well as mid-chain monomethyl alkanes represented by the C19 - C24 homologous with a maximum at C24 hydrocarbon (Melenevskii et al., 2009).

A very similar study on pyrolysis of asphaltene extracted from Venezuelan crude oils showed abundant n-alkenes and n-alkanes with C25 – C33 homologous predominating and a small relative abundance of low molecular weight C8 - C14 n-paraffins (Galarraga et al., 2007). In the later study, the proportion of polar compounds in asphaltene pyrolysate was about ten times higher in crude oils and the values of triaromatic compounds were five times higher than in other crude oils. The total ion chromatograms (TIC) were also compared with the blank chromatograms of individual minerals to identify any blank peak/contaminant in the pyrolysis products chromatograms (Fig. 4 and 5). The outstanding peak (C14) in m/z 91 fragmentogram is subjected to the impact of tropylium ion (possibly co-elution with tropylium ion) resulting from the rescheduling of alkyl substituted benzene ring as shown in Fig. 2D.




TIC: Coal sample
Abundance
(B)
C4
C1
C2
C3
C5
C6
C7
C8
C9
C10
C11
C12
C14
C16
C18
20
22
24
26
28
30
32
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90.00
100.00
110.00
Time-->

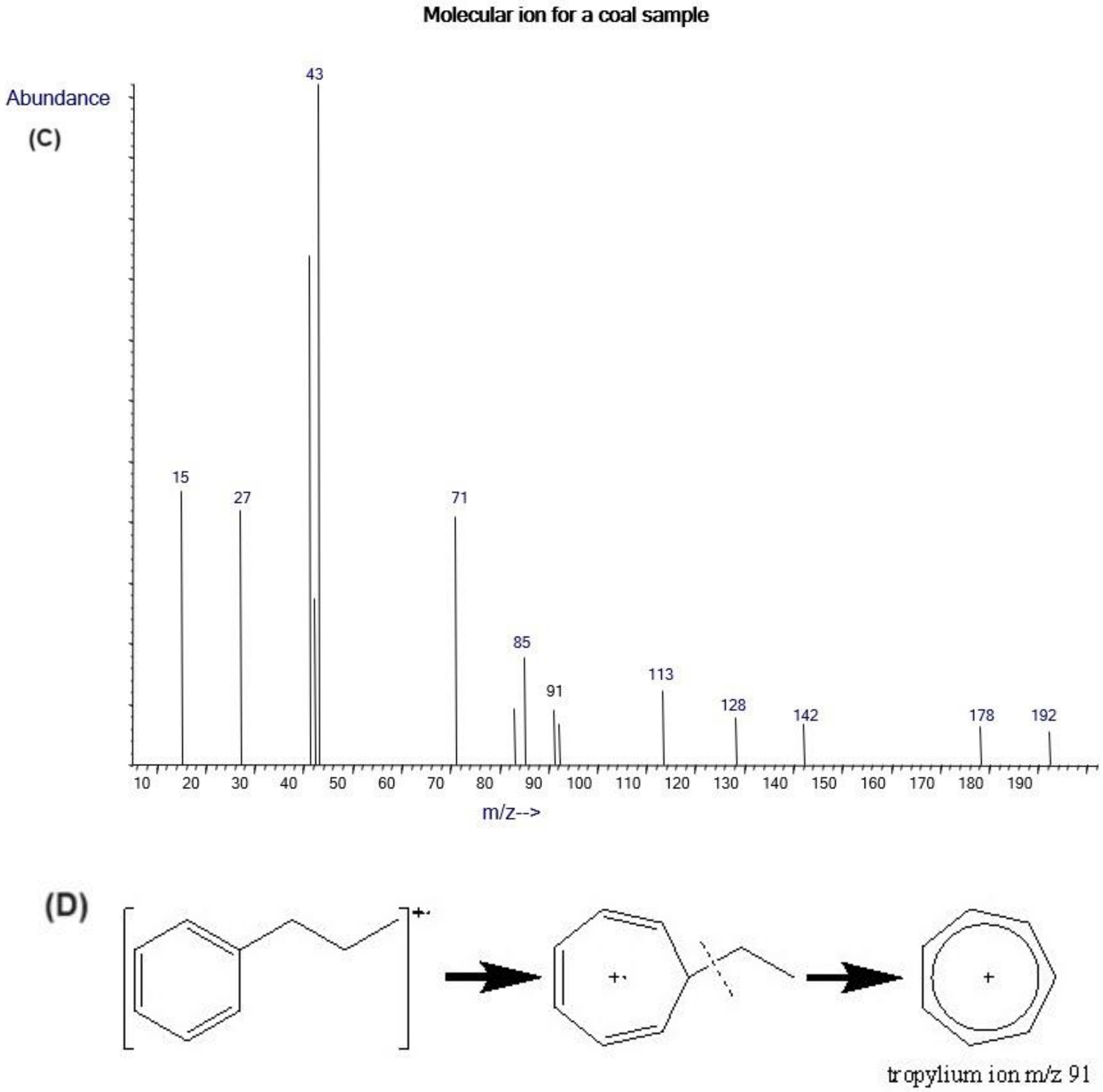


Figure 2: A- Pyrolysis -TIC of asphaltene adsorbed on silica at 850°C, B- Pyrolysis - TIC of a coal reference sample; C- Molecular ion chromatogram of a coal sample for peak identification, D- Rearrangement of alkyl benzene to produce tropylium ion

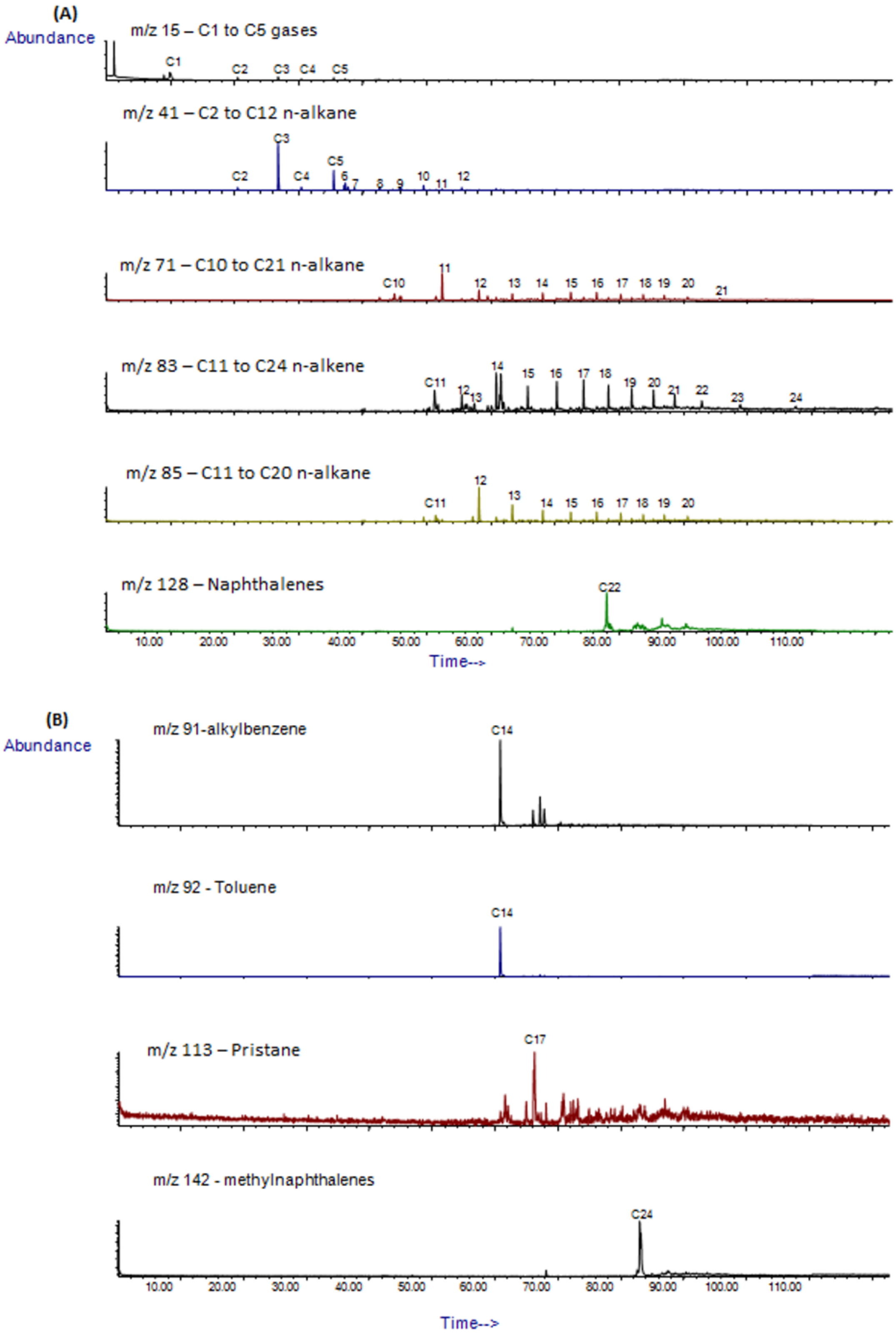


Figure 3: Mass fragmentogram of the pyrolysates (A) and (B) of asphaltene adsorbed on silica and pyrite respectively.

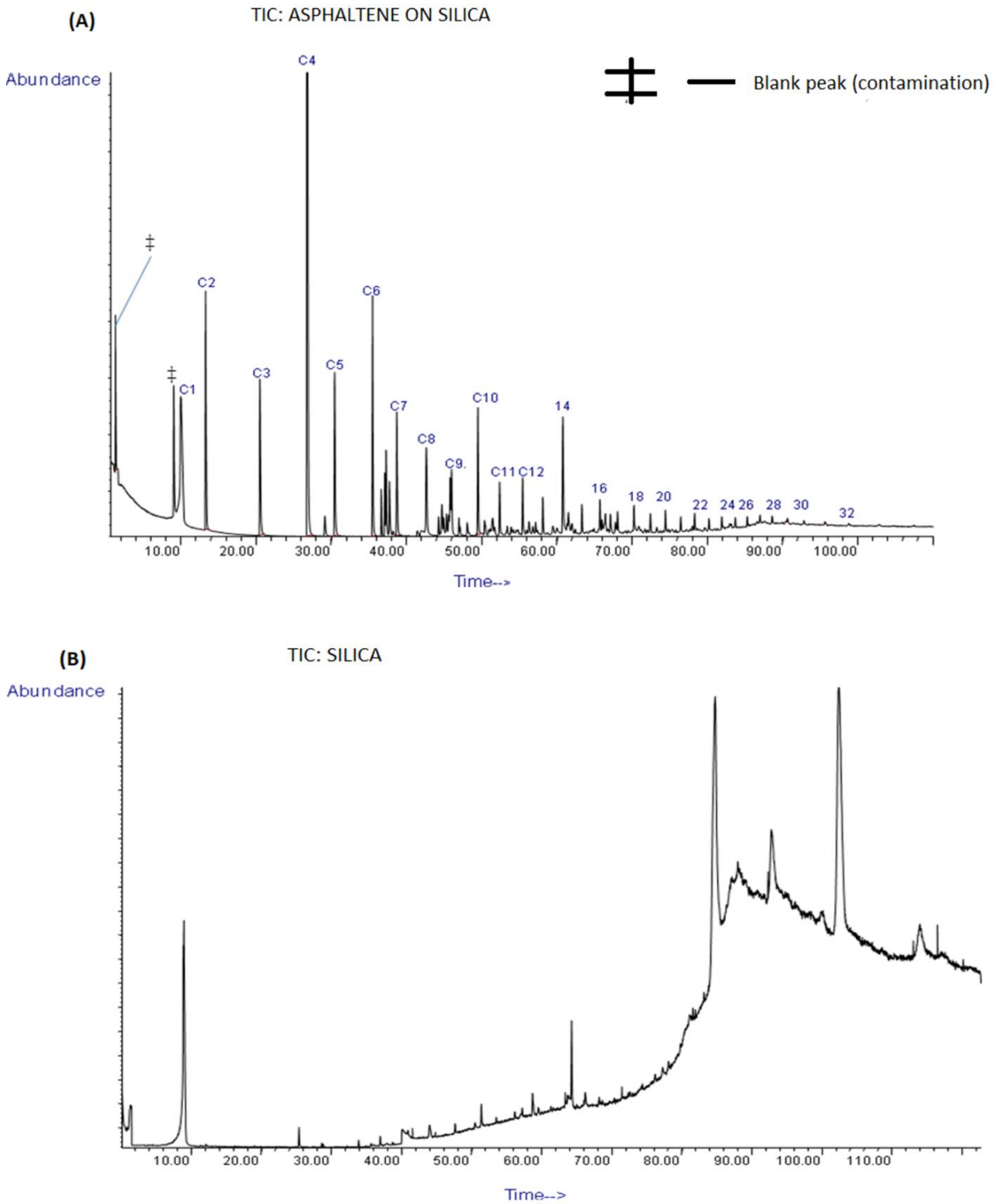


Figure 4: Mass chromatogram of asphaltene adsorbed on silica gel (A) and asphaltene-free silica gel (B)

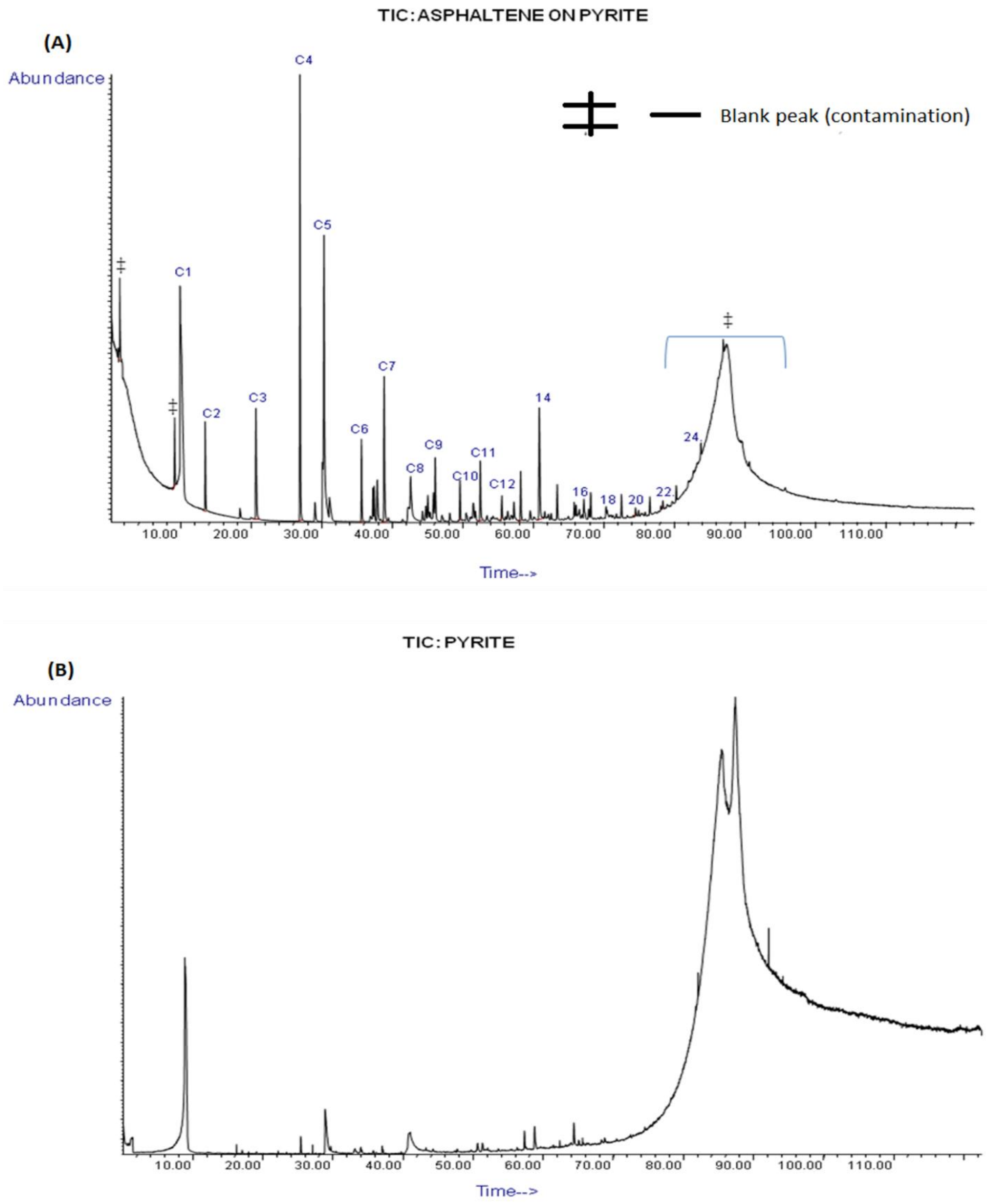
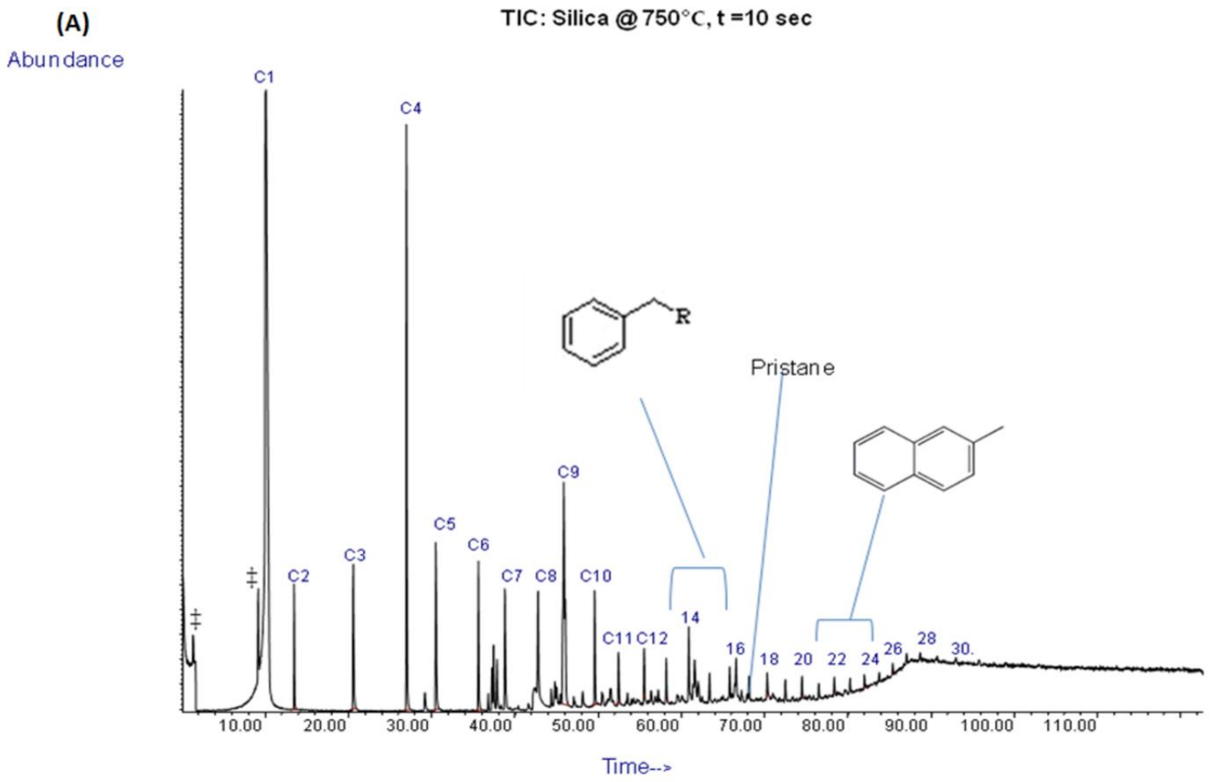


Figure 5: Mass chromatogram of asphaltene adsorbed on pyrite (A) and of asphaltene-free pyrite (B)

For comparative purposes, a few total ions mass chromatograms (TIC) for silica and pyrite adsorbent at different temperatures and equal heating times are discussed based on figures 6 to 8. Based on visual observation of the selected pyrolysis output, it is obvious that in this analysis there is a decrease in yield with the increase in temperature for both silica and pyrite. While there is a gradual decrease of pyrolysates with silica adsorbent; there is a complete disappearance of products like naphthalenes and their derivatives (C21 – C24) in pyrite adsorbent at 850° C and 1000° C. Further integration of these chromatograms showed that pristane is only available in silica adsorbent and present in negligible amounts to completely missing in pyrite adsorbent. The possible reason for the diminishing of products with pyrite may be due to cracking induced by the catalytic consequence of the thermal effects of pyrite (Ma et al., 2016).


(A)
TIC: Silica @ 750°C, t =10 sec
Abundance
‡
‡
C1
C2
C3
C4
C5
C6
C7
C8
C9
C10
C11
C12
R
Pristane
14
16
18
20
22
24
26
28
30.
10.00
20.00
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50.00
60.00
70.00
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90.00
100.00
110.00
Time-->

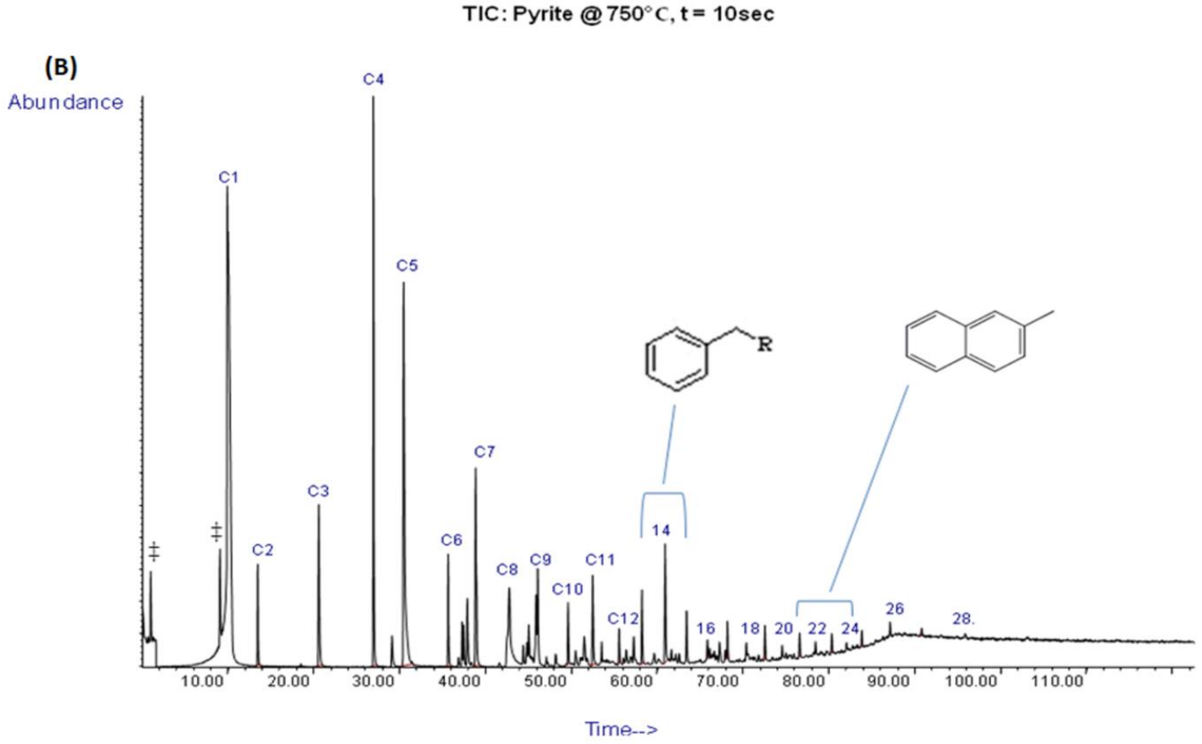

TIC: Pyrite @ 750°C, t = 10sec
(B)
Abundance
‡
‡
C1
C2
C3
C4
C5
C6
C7
C8
C9
C10
C11
C12
R
14
16
18
20
22
24
26
28.
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
90.00
100.00
110.00
Time-->

Figure 6: Total ion chromatogram for asphaltene adsorbed on silica (A) and pyrite (B) at a pyrolysis temperature of 750°C with 10-sec heating duration

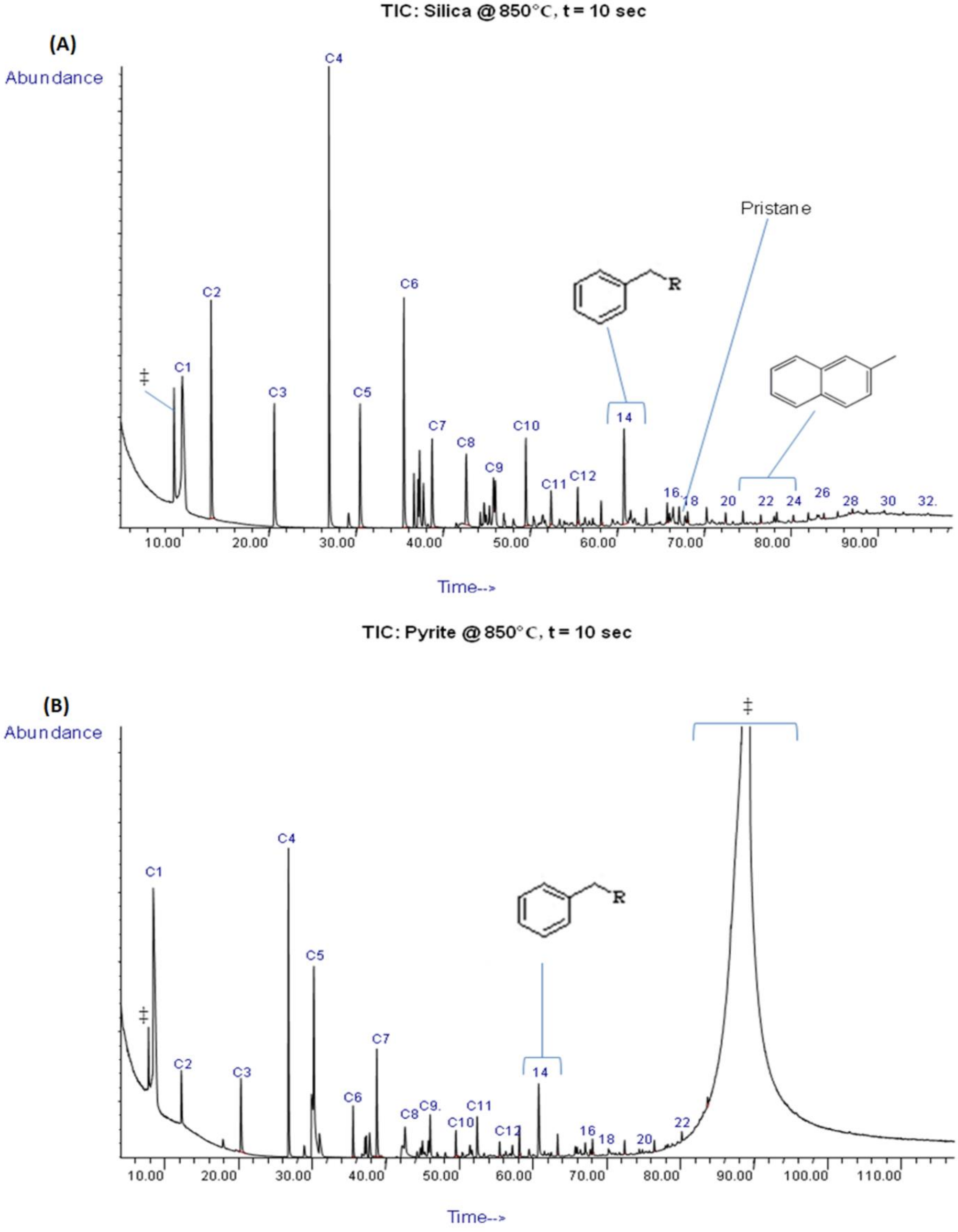


Figure 7: Total ion chromatogram of asphaltene adsorbed on silica (A) and pyrite (B) at a pyrolysis temperature of 850°C with 10 sec heating duration.

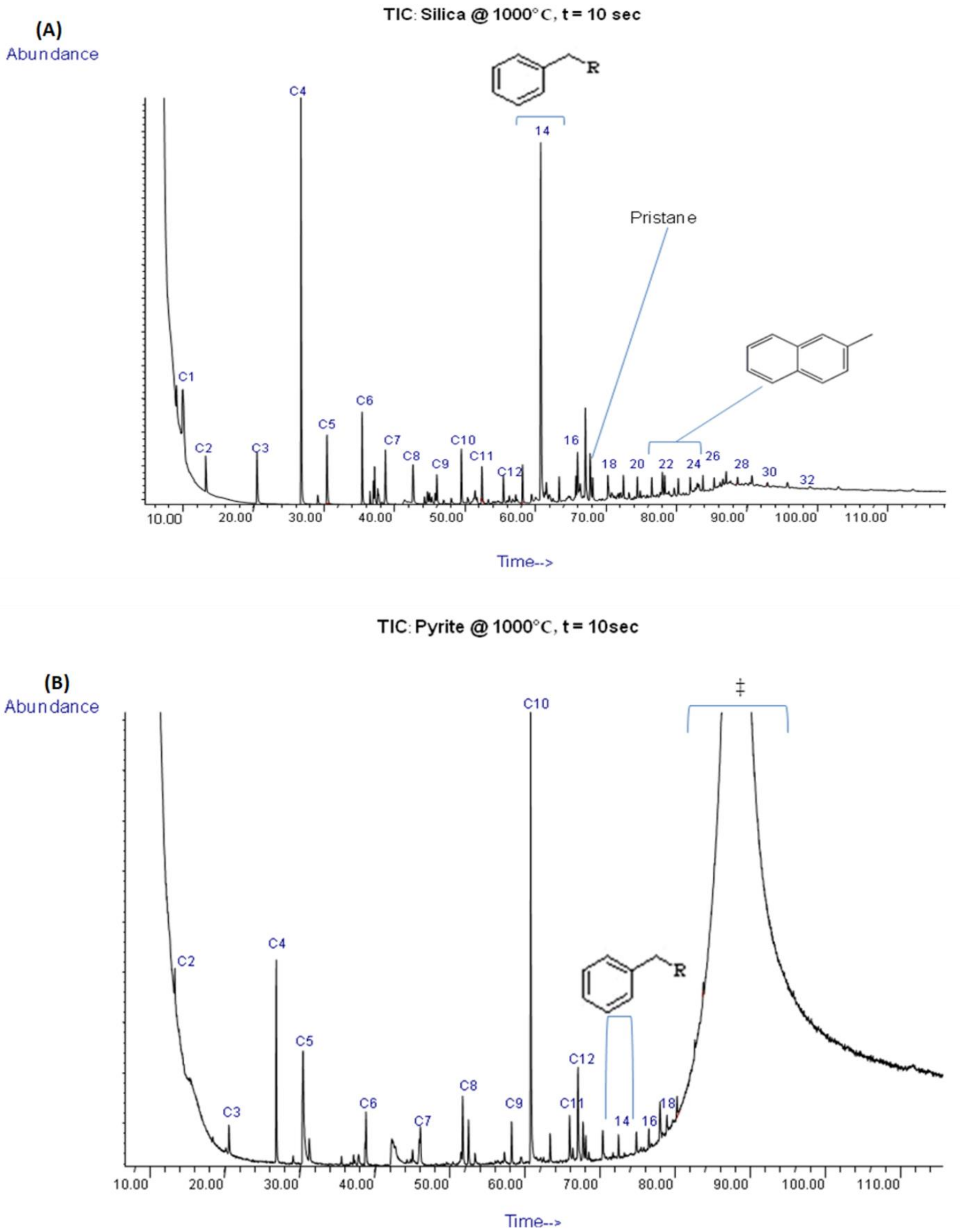
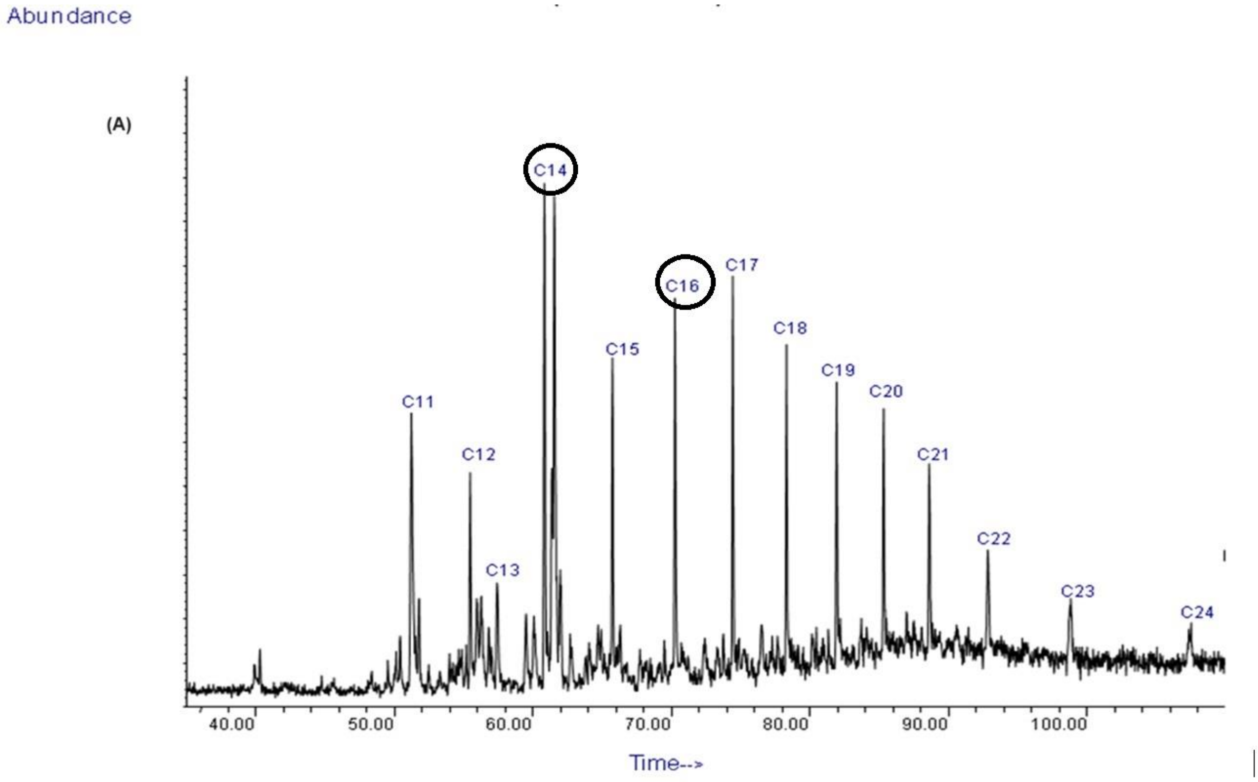


Figure 8: Total ion chromatogram of asphaltene adsorbed on silica (A) and pyrite (B) at a pyrolysis temperature of 1000°C with 10-sec heating duration

3.2 Comparison of pyrolysates of asphaltene adsorbed on silica and pyrite

The fragmentogram for n-alkanes (m/z 85) and n-alkenes (m/z 83) at different temperatures (750° C, 850° C, and 1000° C) and duration-time (8 sec, 10 sec, and 15 sec) were selected for comparison of the peak area ratios. The C14 / C16 ratio was calculated for n-alkene and C12 / C14 ratio for n-alkane (Fig. 9A & B) respectively. The differences between pyrolysates of asphaltene adsorbed on silica and pyrite are assessed using a set of area ratios of selected peaks in the chromatogram, ratio of pyrolysates over the amount of asphaltene pyrolyzed (yield of product) and ratios of various pyrolysates. To apply this technique, multiple ratios were carried out for consistency. All these ratios were plotted against temperature and time to find the distinctive visual patterns between the two-matrix feedstock (silica and pyrite) to enable understanding and detection of any effect caused by the adsorbent/feedstock (Fig. 10 **–** 14).

m/z 83 for n-alkenes



m/z 85 for n-alkane

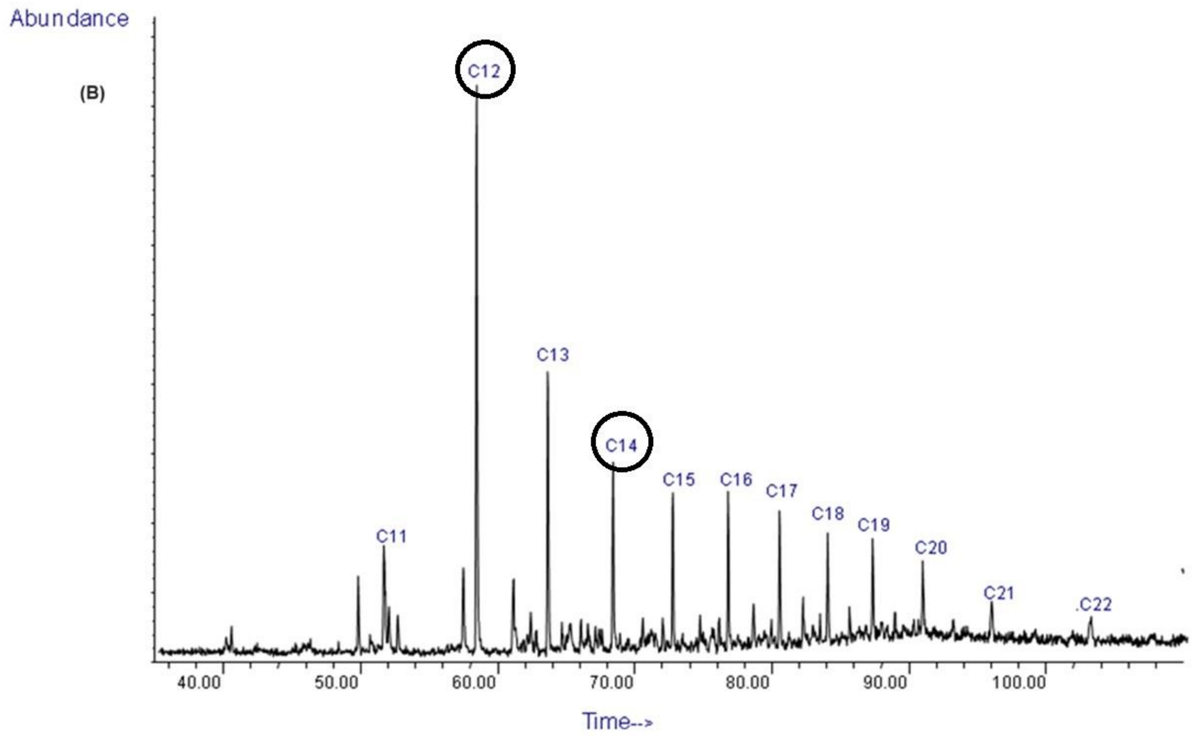


Figure 9: Mass chromatogram of n-alkene (a) and n-alkane (b) used for calculating peak area ratios required for assessing the impacts of mineral matters during pyrolysis.

3.3 Interpretation for silica and pyrite effects based on pyrolysis temperature and heating duration (time)

3.3.1 Asphaltene response during pyrolysis

The pyrolysis of asphaltene often corresponds to the notable mass loss (thermal cracking) of asphaltene that starts at a temperature of 400° C and usually involves the breaking of alkyl groups that weakly bond the poly-aromatic basic units (Goncalves et al., 2001, AlHumaidan et al., 2015). During interpretation of results, figures 10 and 11 showed matrix feedstock effects relying on the product ratios only to pyrolysis temperature; the yield for some products was also calculated by dividing the peak areas of the selected product (n-alkane, n-alkene, total n-alkane and methane) by the amount of asphaltene pyrolyzed and the results were compared to determine the pyrite and silica adsorbent effects caused in the pyrolysates (Fig.12). Asphaltene has a complex reaction pathway that can be affected by a catalyst, temperature, heating duration (time), and even pressure. So, understanding the effects of these factors provides the best approach to asphaltene reactions during pyrolysis and therefore supports the formulation of simulation ideas. Calemma et al., 1997 tested many asphaltenes and the methane gas formation rate indicated a shoulder at higher temperatures which implies that the generation of methane might be through two reaction pathways.

3.3.2 Pyrite and silica adsorbent on asphaltenes

The fragmentogram study of adsorbent-free asphaltene to silica (SiO_2) (Fig.4B) and pyrite (Fig. 5B) at m/z 15 showed the occurrence of methane peaks in pyrite; which is a clear indication for the presence of organic impurities while no any significant peak observed in silica. The disintegration of pyrite occurs in multi-step processes and is largely affected by the availability of organic matters (Gryglewicz et al., 1996; Zhao et al., 2015) and other parameters such as particle size, reaction temperature, time, gas flow rate or diffusion resistance, and sulfur-generated gas phases (Boyabat et al., 2003; Chen et al., 2000; Hu et al., 2006; Zhao et al., 2015). The results showed abnormal peaks between a retention time of 80 and 100 minutes in the pyrite experiments (Fig. 5A) above 850° C; this is believed to be the baseline in the blank asphaltenes-free pyrite pyrograms (Fig.5B) though can also be attributed by the conversion of pyrite to iron (Fe) via a sequence of transformation from pyrite → pyrrhotite → troilite → iron at the temperature of about 950° C in inert environment (Chen et al., 2000; Gryglewicz et al., 1996; Huizinga et al., 1987; Zhao et al., 2015). It is also evident from coal samples of different experiments that; at a temperature above 300 °C, pyrite (FeS_2) converts to pyrrhotite (Fe_7S_8,) and accounts for being a significant catalyst that enhances free radical concentration (Srinivasan, G., and Seehra, M. S. 1983). At earlier temperatures, pyrite was observed to convert to pyrrhotite and even under hydrogen treatment is more effective in producing free radicals than pyrrhotite as observed in this study. This implies that the iron vacancies in pyrrhotite are accountable for its catalytic role.

3.3.3 Thermal decomposition of asphaltenes and their pyrolysates

The assessment of quantitative data is significant in distinguishing compositional changes caused by mineral adsorption effects, thermal alteration of organic matters, and potential enhanced alteration due to the thermocatalytic behavior of minerals (Ishiwaratari et al., 1977). Thermal alteration of asphaltene is considered to be the most essential route for the production of n-alkane and acyclic isoprenoids (pristane) though the free radical dominated thermal cracking of n-alkane and acyclic isoprenoids is fairly slow compared to other generative processes accountable for the production of these hydrocarbons (Ishiwaratari et al., 1977) and acyclic isoprenoids (pristane) are completely destructed by the thermal effect that increased with the addition of the pyrite (Fig. 6B – 8B). This suggests that; the addition of pyrite minerals strongly alters acyclic isoprenoids and are more vulnerable to thermal fracturing than n-alkanes (Ishiwaratari et al., 1977; Waples, 1978). The absence of hydrogen sulfide in the pyrolysates is a good indication of the deficiency of sulfide/polysulfide moieties in the asphaltene fractions (del Rio et al., 1993).

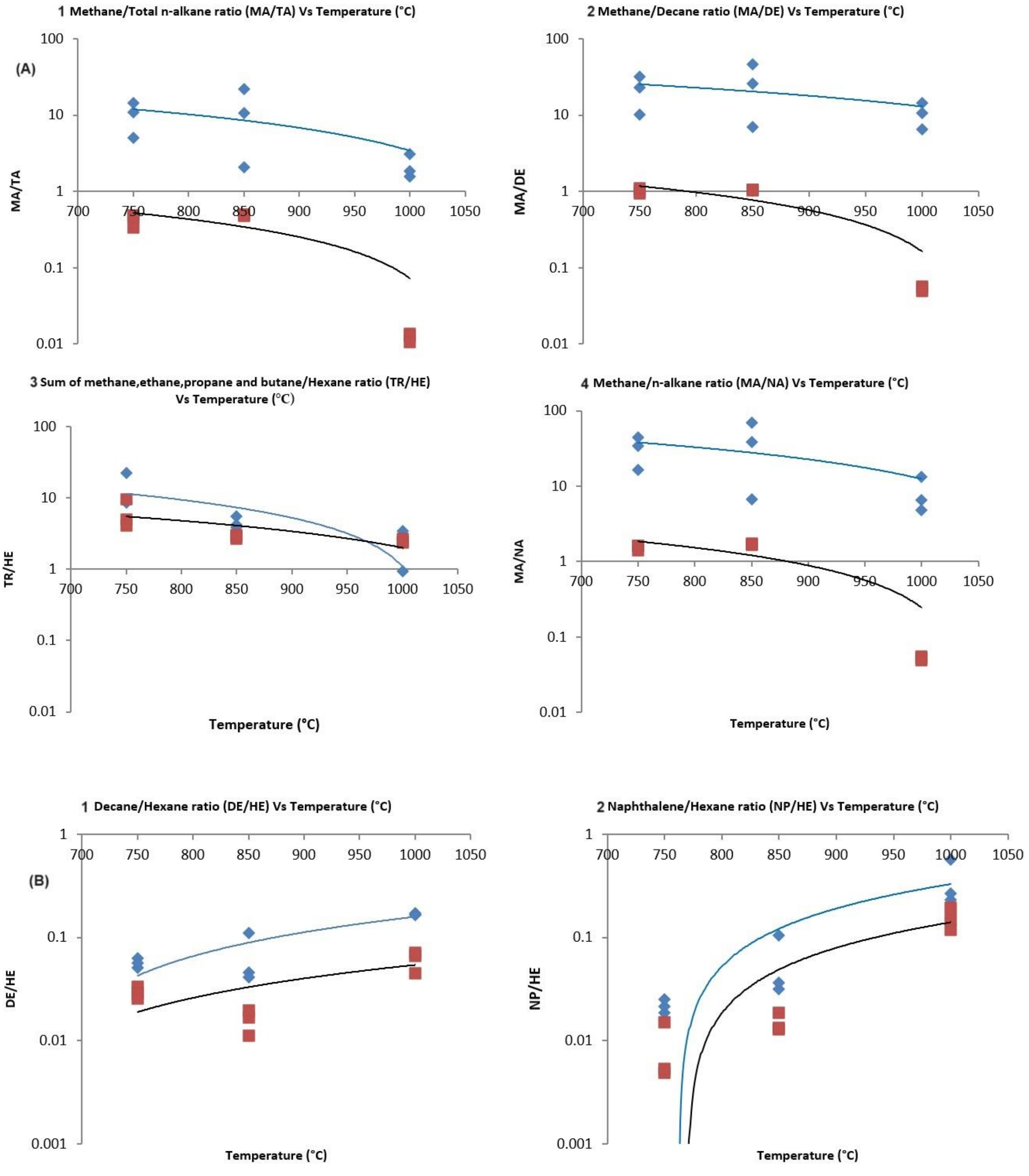


Figure 10: Trends of different ratios with temperature (a) methane to total n-alkane and (b) decane to hexane and naphthalene to hexane ratios used for assessing mineral matrix feedstock effects during pyrolysis

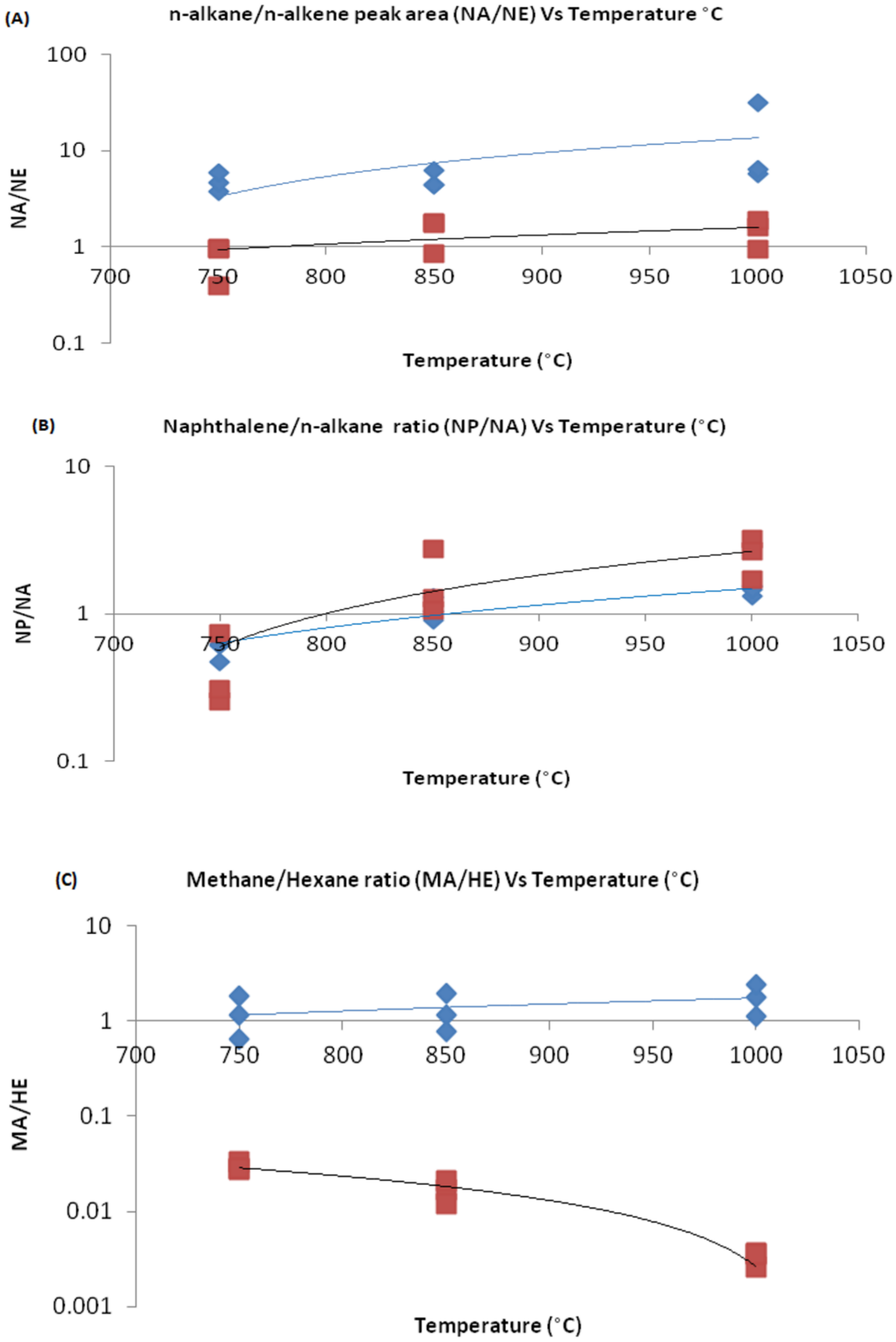


Figure 11: Pyrolysate ratios with temperature (A) n-alkane to n-alkene (B) naphthalene to n-alkane and (C) methane to hexane used for assessing mineral matrix feedstock effects during pyrolysis

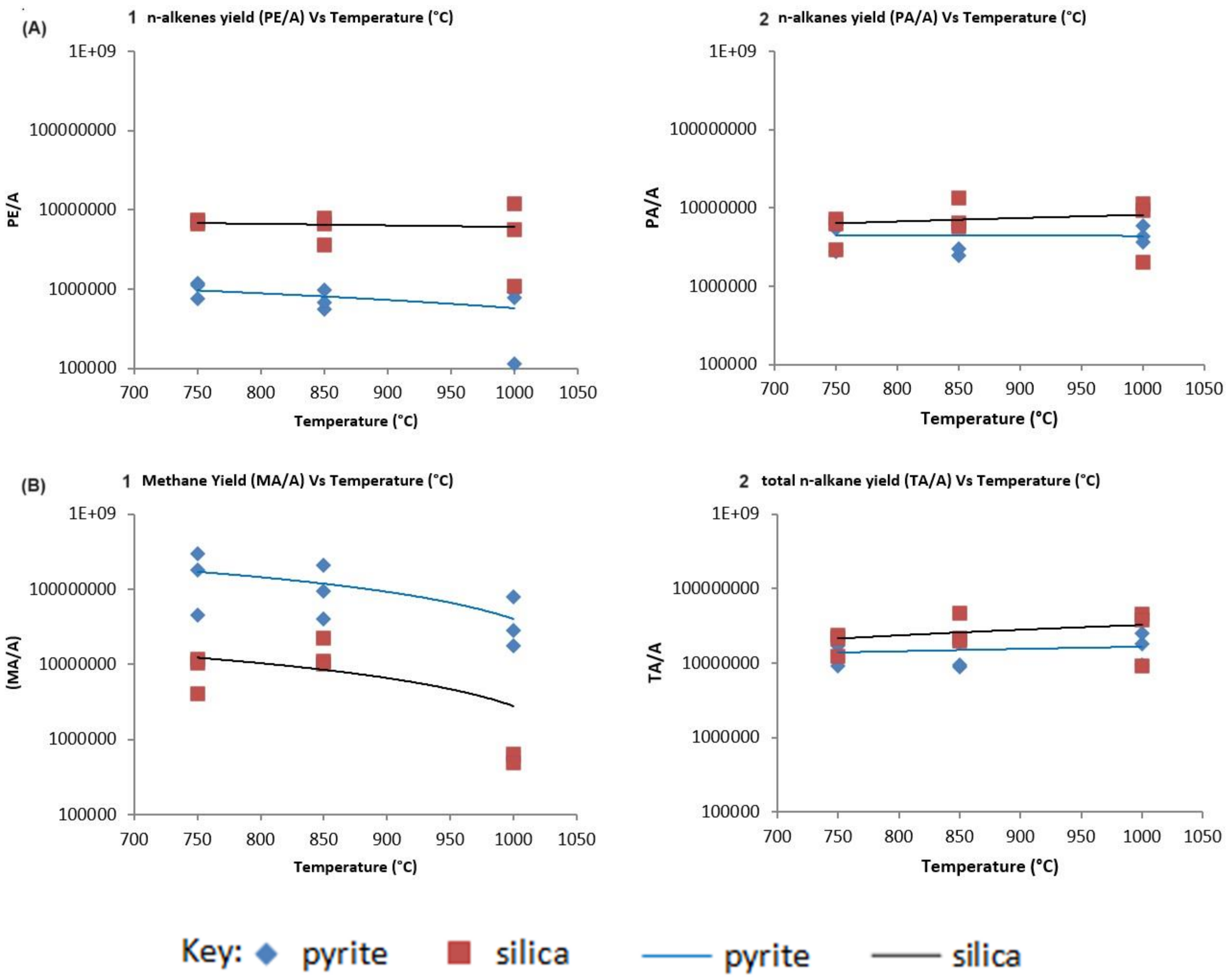


Figure 12: Correlation between silica and pyrite adsorbent effect on some pyrolysis yield

3.3.4 Interpretation of the pyrolysis yields

It has been noted that; the heated asphaltene with pyrite yields significantly higher quantities of methane gas of up to 10 times higher than heated asphaltene with silica (Fig. 10A1, A2, A4, 11C, 12B1), slightly lower total n-alkane (Fig. 12B2), lower n-alkane and much lower n-alkene ratios compared to silica and all products decrease progressively with increase in temperature except for n-alkanes (Fig. 12A2 and B2) which seem to be almost constant. As mentioned earlier, pyrite proved to contain organic impurities which favor its decomposition; therefore, it stimulates the alteration of n-alkane leading to the near destruction of intermediates to high molecular weight compounds in asphaltene (Ishiwaratari et al., 1977) and also promotes the dissociation of initial weak bonds to produce more reactive radicals which eventually causes the rise of methane gas and reduction of other compounds (Geng et al., 2020). Pyrite is confirmed to have a catalytic role in coal liquefaction and gasification processes (Chen et al., 2000; Hu et al., 2006); therefore, in this study, pyrite induces catalytic effects on the pyrolysate. Has been reported that in the pyrolysis of Beypazari oil shales the catalytic role of pyrite was not clear (Ballice, 2005) and the absence of pyrite caused a slight decrease in volatile hydrocarbons (Sert et al., 2009). These effects are significant in maintaining a pyrolysate in contact with potentially reactive mineral surfaces which is a detrimental condition in terms of reducing secondary pyrolysis effects. In this work, silica was observed to delay the thermo-vaporization of non-polar species like n-alkanes at a lower temperature which is why it has insignificant effects on the pyrolysate. The pyrolysate reactions of silicate minerals showed the catalytic effects of silicate minerals aiding the coking reactions and inhibiting conversion to volatile hydrocarbons while the removal of silicates increased the recovery of hydrocarbon yield of oil shales (Sert et al., 2009). The presence of silicate minerals during pyrolysis reduces the diffusion of pyrolysate through the mineral matrix and such experiments showed that pyrolysis reactions were inhibited by silicates and the inhibition effects of the silicates appeared to be greater than the catalytic effects of the carbonate minerals in the pyrolysis reactions (Ballice, 2005, Sert et al., 2009). The explanation for such lower n-alkenes pyrolysate (Fig. 12A1) is unclear though it is evident that pyrite condenses alkenes formation during pyrolysis. Some researchers reported that; when retention of gaseous pyrolysates like hydrogen, hydrocarbon gases, and H_2S are sufficiently high during the experiment in a closed system, the deactivation of free radicals by hydrogen radicals or by recombination may occur and prevent significant alkenes formation (Ishiwaratari et al., 1977; Monthioux et al., 1985).

3.3.5 Interpretation from hydrocarbon peak ratios

The interpretation from peak ratios revealed that the ratio of the sum of light hydrocarbons (C1 - C4) to hexane shows nearly similar effects on both asphaltenes adsorbed on pyrite and silica, and the ratios are shown to decrease gradually with an increase in temperature with little differences in quantities (Fig. 10A3). The unexpected increase of n-alkane to n-alkene ratio with temperature (Fig. 11A) suggests that; under pyrite the n-alkenes are converted to n-alkanes by reaction with hydrogen or to other higher molecular compounds through polymerization reactions (Tannenbaum and Kaplan, 1985). The concentrations of ethene and propene were significantly higher and the ethene to ethane and propene to propane ratios raised in alkane production with pyrite adsorbent though the ethene to ethane ratio was lower than the propene to propane ratio and both ratios were observed to decrease with an increase in temperature (Ma et al., 2016). In the study of the pyrolysis behavior of coal-related compounds, pyrite was also observed to increase the conversion of model compounds and the yield of liquid and gas while decreasing the char yield because after adding the pyrite the large radicals were stabilized on the surface by adsorption forming little chance to combine to form char (Geng et al., 2020).

The quantity of naphthalenes in both cases in the pyrolysate was observed to increase with increasing temperature though with significant differences between the pyrite and silica adsorbents for both naphthalene to n-alkane ratio (Fig. 11B) and naphthalene to hexane ratio (Fig. 10B2). The naphthalene to n-alkane ratios in silica are a little bit high compared to pyrite adsorbent. The reason for this is uncertain; it might be that, silica enhances the generation of naphthalene, and/ or n-alkanes are rigorously altered by thermal catalytic effects of pyrite. The result of this is the destruction of mid to molecular high-molecular-weight compounds that favor naphthalene formation and also this can be attributed to the inhibition effect of the silicates (Sert et al., 2009). Nevertheless, naphthalene-to-hexane ratios under pyrite are high compared to silica; the reason for this is also debatable. It might be because cyclization and aromatization reactions during hydrogen-generating processes are favored by the thermal catalytic effects of pyrite adsorbent compared to silica and/or hexane is an unstable compound. So, it is easily broken down or converted to other products leaving a chance for more generation of naphthalene. The decane-to-hexane ratio (Fig. 10B1) is shown to increase with increasing temperature for both pyrite and silica adsorbents. In this case, pyrite seems to improve the production of aliphatic hydrocarbons with extended heating through a progressive rise in temperature. In coal-related model components pyrolyzed showed an increase of ethylbenzene, styrene, diphenylmethane, and benzene together with other types of liquid products. The quantity of benzene, ethylbenzene, stilbene toluene, and phenanthrene increased while styrene and diphenylmethane decreased as reported by Geng et al., 2020 when there is an increase in temperature with pyrite.

3.3.6 Comparison of pyrolysates of asphaltenes in silica and pyrite adsorbent

In this study, intensive thermal degradation of asphaltene occurred at 850° C where significant changes were observed in the pyrolysate. The formation of alkylbenzene can be attributed to the degradation of sulfur compounds by the thermal catalytic effects of pyrite adsorbent (Tannenbaum and Kaplan, 1985). The ratio of n-alkane to n-alkene was observed to remain constant with increasing duration of heating in silica adsorbent but increases nearly 10 times higher in pyrite adsorbent (Fig. 13A) because, with lengthened heating time, alkenes become minor yield compared to the complimentary alkanes (Ishiwaratari et al., 1977). In other studies (Ma et al., 2016), the saturated hydrocarbons, aromatic hydrocarbons, and non-hydrocarbons were observed to increase by pyrite effects of which the aromatic hydrocarbons became three times larger at 300 ° C indicating that pyrite can cause poly-reaction of alkane while the increase of non-hydrocarbons suggesting that the metallic ions infiltrate the crystalline compounds consisting of metal ions (Ma et al., 2016). Along with this, the chemical activity of pyrite was reported to increase with the increase in the heating temperature.

It has been noted that the ratio of naphthalene to n-alkane and naphthalene to hexane pose minor differences in the level of aromaticity in the pyrolysate of silica and pyrite adsorbent (Fig. 13B and 14C). However, silica enhances aromaticity and the aromatic hydrocarbon is destructed with longer heating (Lui and Kaplan, 1989) possibly due to the cracking off side chains on aromatic compounds with continued heating while in pyrite there is no major effect seen with changes in heating duration except at 850° C where there is an increase in naphthalene (Fig. 14C). In fact, there is insignificant matrix interaction (silica and pyrite) effects on naphthalene production caused by changes of heating time in both silica and pyrite adsorbent.

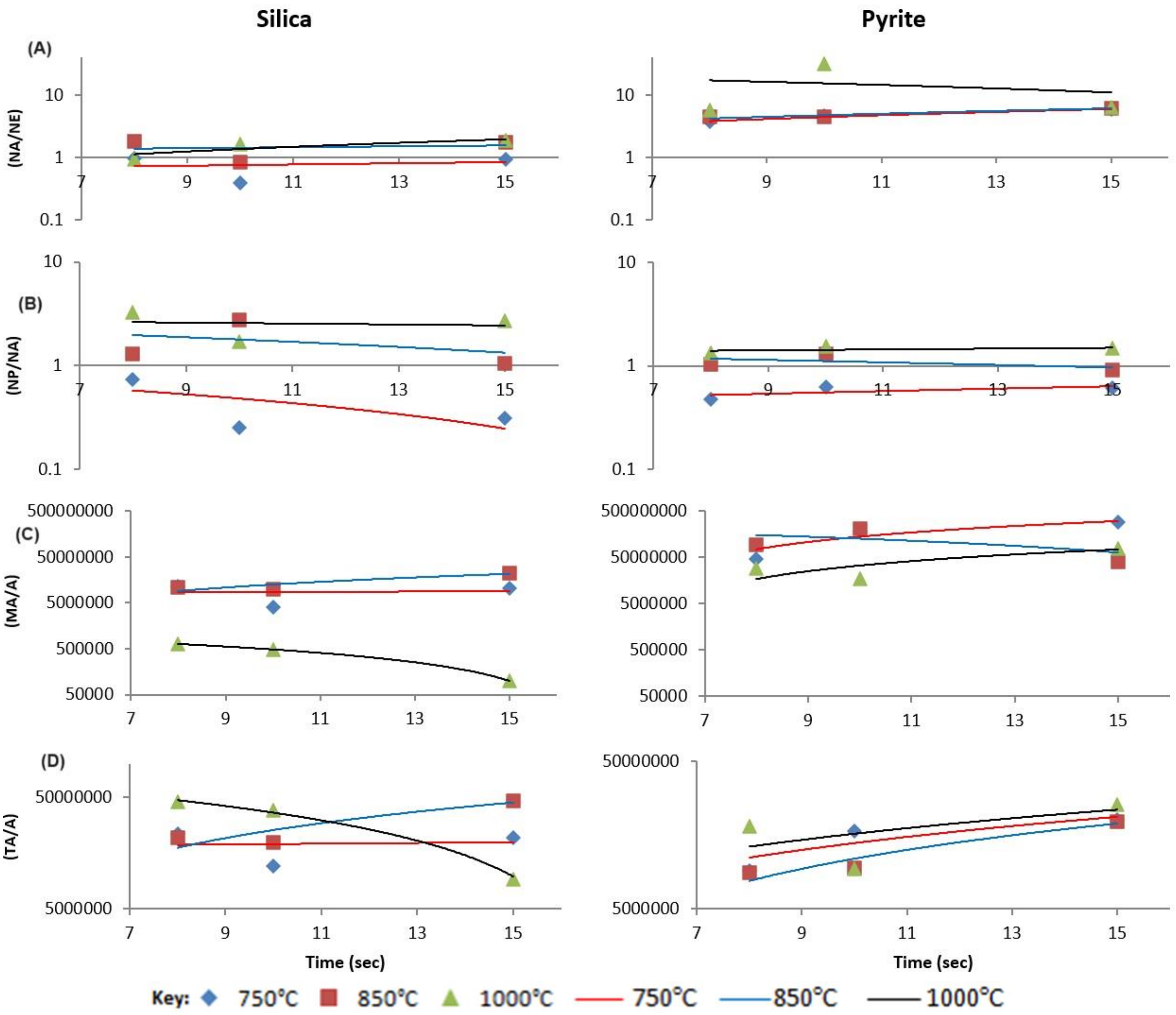


Figure 13: Comparison of pyrolysates between asphaltene adsorbed on silica and pyrite at various heating times, (A) n-alkane to n-alkene ratio, (B) naphthalene to n-alkane ratio, (C) methane yield and (D) total n-alkane yield to assess the mineral matrix feedstock effects during pyrolysis

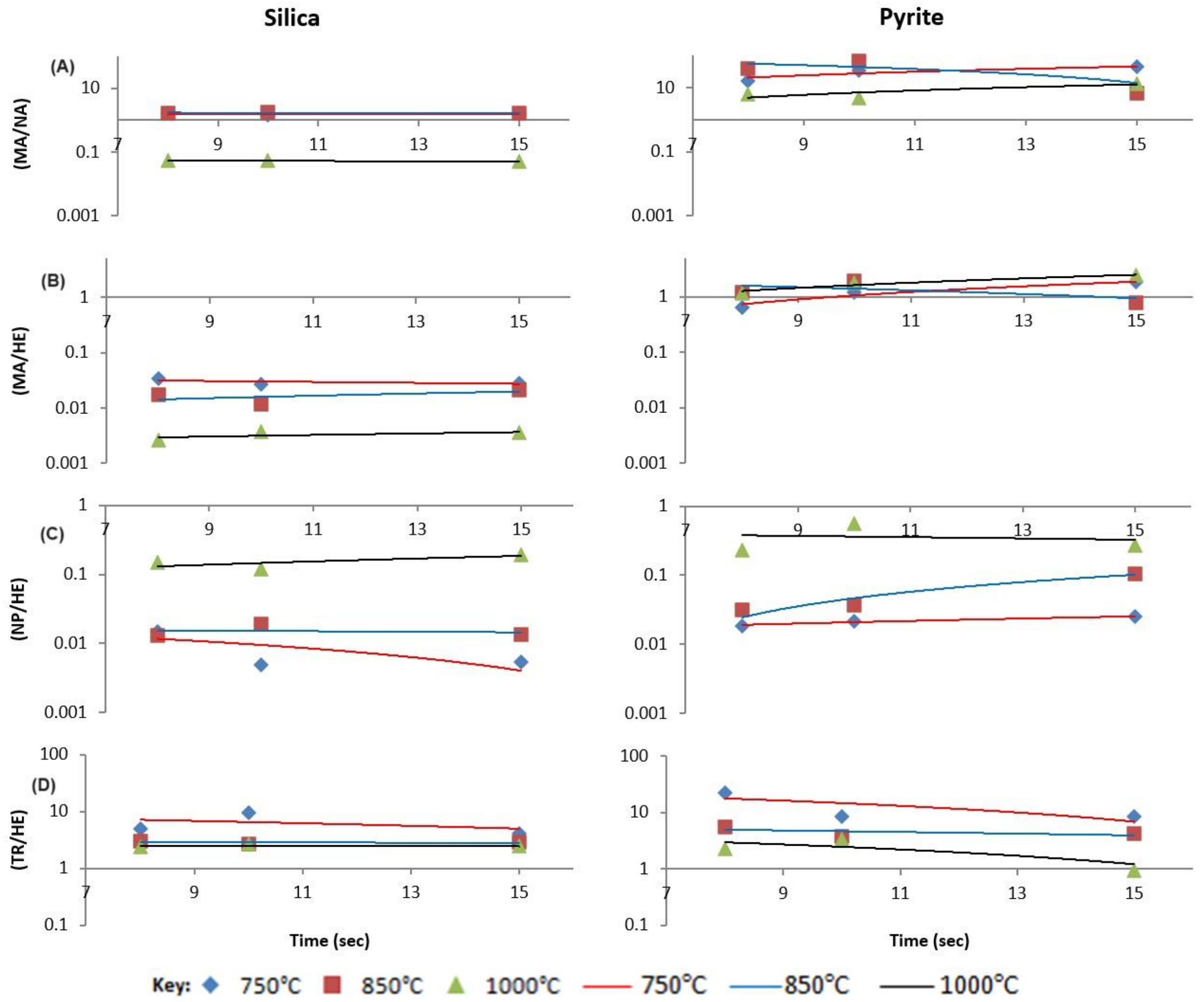


Figure 14: Comparison of pyrolysates between asphaltene adsorbed on silica and pyrite at various heating times, (A) methane to n-alkane ratio (B) methane to hexane ratio, (C) naphthalene to hexane ratio and (D) sum of light gases (C1 - C4) to hexane ratio to assess the mineral matrix feedstock effects during pyrolysis

3.3.7 Generation of methane gas and other hydrocarbons during pyrolysis of asphaltenes

In this paper, methane yield was shown to increase with increasing heating time for both silica and pyrite adsorbents but slightly dropped at 1000° C on silica adsorbent (Fig. 13C). With prolonged heating time, methane to hexane ratio became low in comparison to methane to n-alkane ratio. Similarly, in one of the coal pyrolysis (Geng et al., 2020) the number of gaseous compounds like H_2, CH_4, C_2H_4, and C_2H_8 increased with pyrites adsorbent. In this study, the production of methane gas makes the methane to n-alkane ratio 10 times greater than that of the methane to hexane ratio (Fig. 14A, B) and it was also noted that heating duration has no major effects on silica adsorbent pyrolysate (shown by constant yield) but caused major effects on pyrite pyrolysates which tended to increase (Fig. 14A, B). In other studies (Ma et al., 2016) the influence of pyrites on hydrocarbon generation during pyrolysis, the amount of methane gas, and the sum of C1 - C5 hydrocarbon yields were observed to increase by 50 % except at low temperatures of about 250° C and during such experiments, the amount of methane gas generated in the course of pyrolysis with pyrite was considered to increase from a range of 0.54 – 0.58 to 34.9

- 45.3 ml/g kerogen as temperature was increased from 250° C to 400° C. This suggests that pyrite can enhance hydrocarbon generation by nearly 20 – 50 % at optimum temperature between 250° C to 400° C. The total concentration of C1 – C5 hydrocarbons increased also from 0.860 – 1.09 to 49.5 – 64.2 ml. In general, this study showed that methane gas yield with pyrite adsorbent is 10 times more than with silica adsorbent for extended heating time (Fig.14A, B).

The total n-alkane yield is shown to increase progressively with prolonged heating for both silica and pyrite adsorbent but decreases gradually at 1000° C on silica adsorbent (Fig. 13D) probably due to thermo-cracking effects enhanced by silica adsorbent at high temperatures. Pyrite adsorbent seemed to favor the formation of n-alkanes (aliphatic compounds) for similar reasons explained above. The ratio of the sum of light hydrocarbon gases (C1 - C4) to hexane was shown to decrease slightly with increasing heating time for both silica and pyrite adsorbents and the production rate of these pyrolysates in silica and pyrite adsorbents are comparable (Fig. 14D). This indicates that there are no significant mineral matrix interaction (silica and pyrite) effects on pyrolysates (C1 - C4) caused by changes of heating time (time duration). Other researchers (Ma et al., 2016) showed that the ratios of ethene to ethane and propene to propane decreased with increasing temperatures but increased in under-pyrite-added when pyrite began to decompose; this gives a clear indication that pyrite acts indirectly as a catalytic agent and/or directly as an inducer for sulfur and improves the free radical formation and hydrocarbons generation (Ma et al., 2016).

4. Conclusion

The role of minerals (silica and pyrite) in petroleum generation has been evident through laboratory simulation processes. The study of silica and pyrite interaction on asphaltene during analytical pyrolysis proved that minerals are qualitatively affecting pyrolysate and both temperature and time are prerequisite conditions for the effects observed. There were insignificant effects on pyrolysate with silica adsorbent while there were potential effects on the pyrolysates with pyrite adsorbent almost 10 times higher than in silica as observed in the generation of methane gas. This might be attributed to the catalytic role of pyrite minerals.

The isoprenoid-pristane appeared only when running pyrolysis on silica absorbent and appeared to crack over pyrite adsorbent possibly due to the thermal catalytic of pyrite. Pyrite proved to enhance gaseous and liquid hydrocarbons generations with temperature increase. The significant matrix effects involved the conversion of primary pyrolysate into secondary pyrolysate as observed in the generation of aliphatic hydrocarbons/compounds.

For future work, it is recommended to extend the range of pyrolysis temperature and heating duration with the same or other minerals adsorbents like galena, gypsum, sphalerite, chalcopyrite, pyrrhotite, and clays to establish the benchmark for evaluation of pyrolysis effects.

Acknowledgment

The authors are thankful to the following staff of the University of Aberdeen (UK), for their moral and technical support: Dr. Stephen Bowden, (MSc research supervisor of the first author), Ayad N. Faqi (a PhD Student then), and Colin Taylor and Elizabeth (geochemistry technicians from geochemistry laboratory).

Declarations

Conflict of interest statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Funding statement

No funding

Data availability statement

The datasets generated during and/or analyzed during the current study are available from the corresponding author on request.

Authors' contributions:

All authors contributed to the study's conception and design. Laboratory works and the first draft of the manuscript was performed by Mr. John Kalimenze. The analysis and review of the drafted manuscript were performed by Mr. Benatus Mvile. All authors read and approved the final manuscript. The authors have further agreed that Mr. Kalimenze should submit and be the corresponding author of this paper.

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